4.006 Quantification of gas-wall partitioning in Teflon environmental chambers using rapid bursts of low-volatility oxidized species generated in-situ .

Early Career Scientist

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Abstract:

Partitioning of gas-phase organic compounds to the walls of Teflon environmental chambers is a recently reported phenomenon than can affect the yields of reaction products and secondary organic aerosol (SOA) measured in laboratory experiments. Reported timescales for reaching gas-wall partitioning (GWP) equilibrium (τ_{GWE}) differ by up to three orders of magnitude, however, leading to predicted effects that vary from substantial to negligible. A new technique is demonstrated here in which semi- and low-volatility oxidized organic compounds (saturation concentration c^{*}<100 µg m^{-3}) were photochemically generated in rapid bursts *in-situ*- in an 8 m^{3} environmental chamber, and their decay due to loss to the walls in the absence of aerosol was measured using a high-resolution chemical ionization mass spectrometer (CIMS) equipped with an “inlet-less” NO_3^- ion source. Measured τ_{GWE} were 7-13 min for all compounds, with an average relative standard deviation of 33% for replicate experiments. The fraction of each compound that partitioned to the walls at equilibrium follows absorptive partitioning theory with an equivalent wall mass concentration in the range 0.3-10 mg m^{-3}. By comparison, τ_{GWE} measured using a CIMS equipped with a standard low-pressure ion-molecule reaction region were biased high by up to a factor of 4, and the equivalent wall mass concentrations were biased low. Thus, improved ion sources that reduce the contact of compounds with walls are needed for low-pressure CIMS. On the basis of these results, a set of parameters is proposed for modeling GWP in chamber experiments. We applied these findings to fit the results of an ISOPOOH oxidation study in the Caltech chamber in which we reported a new SOA formation mechanism. The effects of relative humidity and temperature on gas-wall partitioning, and wall losses on SOA experiments in which competing aerosol seed particles are generated in the chamber were also explored.